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Studies in the Stereochemistry of Quinquevalent Nitrogen. V.

The Betaines and the Formation of Unsaturated Acids in Plants. I.

By

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The α-betaines, the pentavalent nitrogen compounds occurring in plants, can be synthesised by the methods which will be described below.

(1) By the ordinary process of methylation with methyl iodide and caustic potash on the α-amino acids :[1]

$$RCHNH_2CO_2H + 3CH_3I + 3KOH = \begin{matrix} RCH\text{———}CO \\ | \qquad\qquad | \\ N(CH_3)_3\text{—}O \end{matrix} + 3KI + 3H_2O.$$

Thus the betaines of α-aminobutyric acid and of phenyl alanine were obtained, while tyrosine by the exhaustive methylation was transformed to the betaine of p-methoxy phenyl alanine.

Aspartic acid however by the same treatment completely breaks up into trimethyl amine and fumaric acid as observed by Körner and Menozzi :[2]

$$HO\cdot C_6H_4CH_2CH(NH_2)CO_2H + CH_3I + KOH \rightarrow \begin{matrix} CH_3O\cdot C_6H_4CH_2CH\text{——}CO \\ | \qquad\qquad | \\ N(CH_3)_3\text{-}O \end{matrix}.$$

$$\begin{matrix} CH_2\cdot CO_2H \\ | \\ CHNH_2CO_2H \end{matrix} + 3CH_3I + 3KOH = \begin{matrix} CH\cdot CO_2H \\ \| \\ CH\cdot CO_2H \end{matrix} + (CH_3)_3N + 3KI + 3H_2O.$$

In other cases, also, by methylation, there was formed an unsaturated acid corresponding to the amino acid together with the betaine, the former having been separated by precipitation from the latter by acidify-

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1 Griess, Ber. D. Chem. Ges., **8**, 1406 (1875); Yoshimura, Bull. Kagoshima. Imp. Coll. Agri. Fores., I., 79 (1915).

2 Gaz. chim. ital., **II**, 2453 (1881).

ing the reaction products with dilute hydrochloric acid. The quantity of the unsaturated acid formed depends upon the nature of the amino acid and is proportional to the time of heating in the methylation.

(2) By subjecting the addition compound of the tertiary amine with an equivalent quantity of the α-halogen acid ester to the action of alkali:

$$R_3N + R'CHXCO_2C_2H_5 = R_3NCHR'CO_2C_2H_5$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad X$$

$$R_3NCHR'CO_2C_2H_5 + MeOH = \begin{matrix} R_3N{-}CHR' \\ | \quad | \\ O{-}CO \end{matrix} + C_2H_5OH + MeX.$$
$$\quad |$$
$$\quad X$$

The author prepared dimethyl phenyl ethyl acetate ammonium iodide, methyl phenyl benzyl ethyl acetate ammonium iodide and l-menthyl acetate pyridinium iodide by mixing the equimolecular quantities of the tertiary amines and iodoacetic esters.

In the preparation of these quaternary ammonium iodides, when dimethyl aniline and methyl benzyl aniline were used, the salts were separated in crystalline state after one and four days respectively. When, however, methyl ethyl aniline or methyl allyl aniline was used, even after two years no solid substance was found to be formed.

The author further attempted to resolve methyl benzyl phenyl ethyl acetate ammonium iodide into its optical antipodes by means of silver dextro-camphorsulphonate in the acetone or ethyl acetate solution, and the white needle-shaped crystals, obtained by the fractional crystallisation of the racemic methyl benzyl phenyl ethyl acetate ammonium dextro-camphorsulphonate in the acetone solution, melted at 178–179°, and gave the specific rotatory power $[\alpha]_D^{25} = +11{\cdot}85°$ in an aqueous solution. After recrystallisation from ethyl acetate, the rotatory power of the same substance was again determined, and observed to be $[\alpha]_D^{25} = +13{\cdot}68°$, which agrees with that of the racemic betaine salt of dextro-camphorsulphonic acid.

The author's endevour to resolve the ammonium salt, however, by means of dextro-bromocamphorsulphonic acid and dextro-tartaric acid, into the optically active compounds has not been succeeded.

Some years ago, E. Wedekind and O. Wedekind[1] succeeded in the preparation of the optically active ethyl tetrahydroisoquinolium betaine

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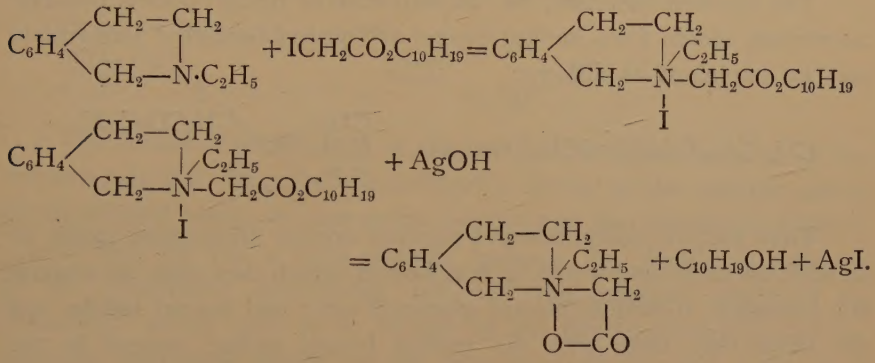
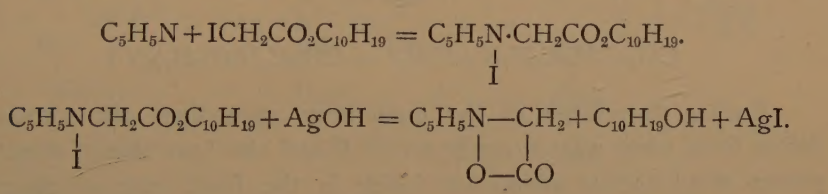
[1] Ber. D. Chem. Ges., **41**, 456 (1908).

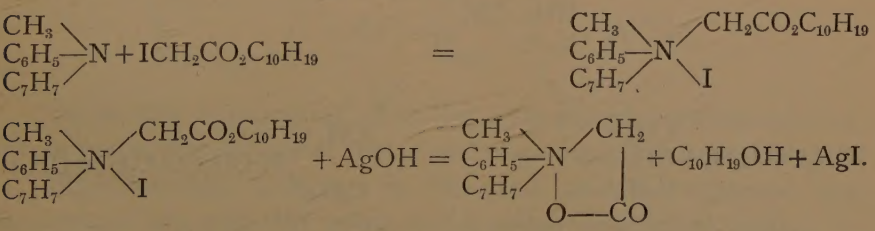
by means of the asymmetric synthesis from n-ethyl tetrahydroisoquinoline and l-menthyl iodoacetate :



The author prepared l-menthyl acetate pyridinium iodide from l-menthyl iodoacetate and pyridine, which by treating with silver hydroxide was transformed into the pyridine betaine :



By the analogy with these reactions, it was anticipated that the optically active methyl benzyl phenyl betaine would be formed by the application of the asymmetric synthesis to methyl benzyl aniline, and the author undertook the investigation expecting that the following reactions may take place :



On allowing the mixture of methyl benzyl aniline and l-menthyl iodoacetate to stand for 4 months in a dark cold place, the colourless crystals were found to deposit. These were separated by filtration from the mother liquor and recrystallised from water and analysed. The substance possessed a composition corresponding to the formula $C_{21}H_{22}NI$

and melted at 108·5–109°, having all the properties of methyl phenyl dibenzyl ammonium iodide.[1]

The reaction therefore, for the formation of methyl phenyl dibenzyl ammonium iodide from methyl benzyl aniline and l-menthyl iodoacetate may be explained as follows:

$$CH_3{\cdot}C_6H_5{\cdot}C_7H_7N + ICH_2CO_2C_{10}H_{19} = \begin{matrix} CH_3 \\ C_6H_5 \\ C_7H_7 \end{matrix}\!\!>\!N\!<\!\!\begin{matrix} CH_2CO_2C_{10}H_{19} \\ \\ I \end{matrix}$$

Thus methyl phenyl benzyl l-menthyl acetate ammonium iodide or an addition compound would be first formed, which then may decompose into l-menthyl n-methyl phenyl glycocoll ester and benzyl iodide, and the latter may unite with the methyl benzyl aniline present in the mother liquor:

$$\begin{matrix} CH_3 \\ C_6H_5 \\ C_7H_7 \end{matrix}\!\!>\!N\!<\!\!\begin{matrix} CH_2CO_2C_{10}H_{19} \\ | \\ I \end{matrix} = \begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!N{\cdot}CH_2CO_2C_{10}H_{19} + C_7H_7I$$

$$CH_3{\cdot}C_6H_5{\cdot}C_7H_7N + C_7H_7I = CH_3{\cdot}C_6H_5(C_7H_7)_2N{\cdot}I.$$

Such a dissociation of the quaternary ammonium salt somewhat differs from what was shown in article I[2] and also from that of dimethyl phenyl ethyl acetate ammonium iodide in the fused state as observed by Wedekind.[3] In the latter case, the double dissociation of the ammonium salt as shown in the following scheme, actually takes place in the fused state. This was confirmed by the author by the thermal analysis and also by the chemical method:

$$\begin{matrix} CH_3 \\ CH_3 \\ C_6H_5 \end{matrix}\!\!>\!N\!<\!\!\begin{matrix} CH_2CO_2C_2H_5 \\ \\ I \end{matrix}$$

$$ICH_2CO_2C_2H_5 + \begin{matrix} CH_3 \\ CH_3 \\ C_6H_5 \end{matrix}\!\!>\!N \qquad \begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!N{\cdot}CH_2CO_2C_2H_5 + CH_3I$$

When, however, methyl phenyl benzyl ethyl acetate ammonium iodide was heated, it decomposed at 103° into methyl phenyl glycocoll

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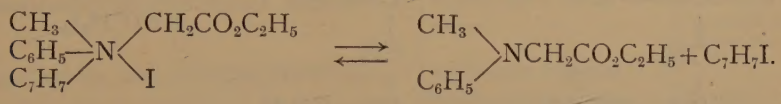
1 Komatsu, Mem. Coll. Sci. Engin., Kyoto, **3**, 406 (1912).

2 *Ibid*, **3**, 372 (1912).

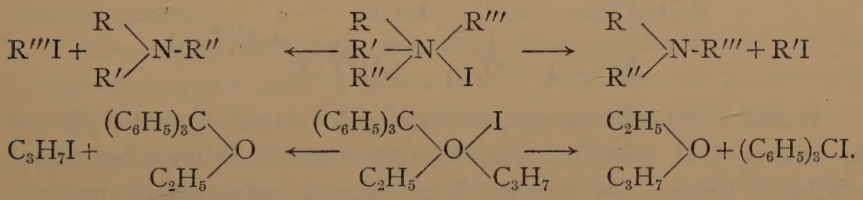
3 Ber. D. Chem. Ges., **35**, 766, 1075 (1902).

ethyl ester and benzyl iodide which on cooling recombined to form the original substance, as is shown in the following scheme:

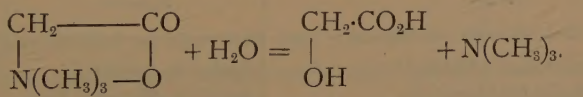


The double dissociation of ammonium salts in a fused state or of the solution may give support to Tschelinzeff's theory[1] of the catalytic action of the tertiary amine or ether in the formation of the Grignard's reagent.

In fact, we find a close analogy between the double dissociation of the quaternary ammonium salt and the reactions observed by Stadnikoff[2] which seem to be caused by the double dissociation of the oxonium compound formed by the interaction of n-propyl iodide and magnesium in the presence of triphenyl methyl ethyl ether, as is shown in the following schemes:



When trimethyl glycocoll (betaine) is heated with potassium hydroxide,[3] it decomposes into trimethyl amine and glycollic acid. The same chemical change was observed by Ehrlich and Lange[4] when the betaine was exposed to the action of a wild yeast like *Willia anomale*:



On heating hypaphorine[5] (trimethyl tryptophane) with concentrated aqueous potassium hydroxide, indole and trimethyl amine were produced.

Ergothionenine,[6] however, by the same chemical treatment was decomposed into trimethyl amine and a yellow unsaturated acid:

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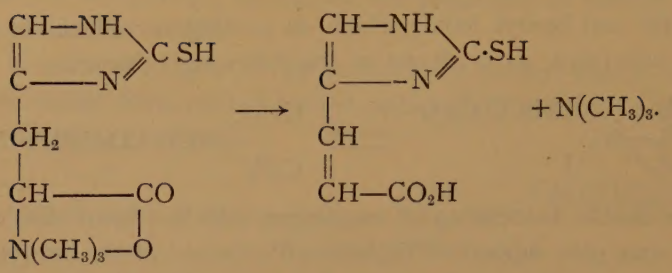
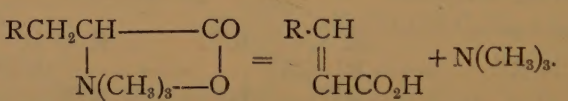
1 *Ibid*, **38**, 3664 (1905); **40**, 1487 (1907).
2 *Ibid*, **44**, 1157 (1911).
3 Abderhalden, Biochem. Handlexikon. IV. 834.
4 Ber. D. Chem. Ges., **46**, 2746 (1913).
5 Romburgh and Barger, J. Chem. Soc., **99**, 2071 (1911).
6 Barger and Ewins, *Ibid*, **99**, 2336 (1911).



The betaines, prepared from the α-amino acids by exhaustive methylation, were subjected to decomposition by heat, as in the case of the quaternary ammonium hydroxide. By this treatment, the betaines were found to decompose into trimethyl amine and α-unsaturated acids; and, actually, α-crotonic acid, cinnamic acid and p-methoxy cinnamic acid were obtained from the corresponding betaines, and the yields were fruitful:



Hence, it is natural to assume that in the course of methylation of the aspartic acid, trimethyl aspartic acid would be formed, but actual isolation a betaine has not yet been effected owing to its unstable nature, spontaneously decompositing into fumaric acid and trimethyl amine.

On referring the literature,[1] we have found the following occurrences of the unsaturated acids in the vegetable kingdom:

Acids	Sources.	Remark.
Methacrylic acid, $CH_2{:}C{\cdot}CH_3CO_2H$.	Anthemis nobilis L.	In oil.
Tiglic acid, $CH_3CH{:}C(CH_3){\cdot}CO_2H$.	Sabadilla officinalis Engl.	Associates with cevine and teloidine.
Angelic acid, „	Sabadilla officinalis Engl. Angelicae radix.	Associates with veratrine.
Sorbic acid, $CH_3CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$.	Sabadilla officinalis Sorbus Aucuparia.	
Fumaric acid, $CO_2HCH{:}CH{\cdot}CO_2H$.	Fumariaceae, Papavaceae.	Associates with papaverine and morphine.

1 Euler: Grundlagen u. Ergebnisse d. Pflanzenchemie. I. (1908); H. Kraemer. Scientific and Applied Pharmacognosy, 1915; Winterstein-Trier: Die Alkaloide, 1910; T. A. Henry: The Plant alkaloids, 1913.

Acids	Sources	Remark
Cinnamic acid, $C_6H_5CH{:}CHCO_2H$. (Allo and iso).	Erythroxylon coca.	Associates with cocaine and ecgonine.
o-Oxy-Cinnamic acid, $OH{\cdot}C_6H_4CH{:}CHCO_2H$.	Angraecum fragrans.	
p- „ „ „	Xanthorrhoea arborea.	In resin.
Caffeic acid, $(OH)_2C_6H_3CH{:}CH{\cdot}CO_2H$.	Conium maculatum.	Associates with conine and melthylconine.
Piperic acid, $CH_2O_2C_6H_3CH{:}CH{\cdot}CH{:}CHCO_2H$.	Piper nigrum.	Associates with piperidine.
Sinapic acid, $(CH_3O)_2{\cdot}OHC_6H_2CH{:}CH{\cdot}CO_2H$.	Brassica nigra.	Associates with coline.

As seen in the foregoing table, the unsaturated acids in plants, are found for the most part to associate with alkaloids—the tertiary amine —although some in a free state or in polymerised form, occur in oil or resinous matter.

Hitherto our knowledge regarding the mechanism for the formation of the unsaturated acids in plants is very poor; but the present study, on the decomposition of the betaines, may present some data for the explanation of the naturel formation of those acids.

If we admit that the changes involved in the natural formation of the unsaturated acids would be analogous to those which take place in the synthetical processes applied in the laboratory, and also that the α- amino acids, the decomposition products of the proteines, and betaines the intermediate compounds in the natural synthesis of the unsaturated acids in plants, we can easily explain the facts met with in nature.

The unsaturated acids, with the exception of certain fatty acids, are all the α-unsaturated compounds and usually associate with the tertiary amines. These facts harmonize with the author's hypothesis concerning the formation of the unsaturated acids in plants.

Moreover the author's work gives support to the view expressed by Dr. Trier:[1] "In gewissen Fällen (Asparaginsäure, Tyrosin, Phenylalanin) scheinen nämlich die primärgebildeten Betaine leicht in Trimethylamine und ein ungesättigte Säure weiter zu zerfallen. Die bis jetzt nach geweiessenen Betaine sind solche, welche, nach ihrem Ver-

1 Trier, Über einfache Pflanzenbasen u. ihre Bezie. z. Aufban d. Eiweißstoffe u. Lecithine. 1912, p. 88.

halten gegen Alkali zu schließen, verhältnismäßig schwer ihren Stickstoff abgeben und daher auch in pflanzlichen Organismus weniger leicht verändert.

"Durch solche Betrachtungen kommen wir dazu, auch für stickstofffreie Pflanzenstoffe, wie etwa die Fumarsäure oder Zimmtsäure eine Entstehung aus dem Eiweiß bzw. seinen Bausteinen anzunehmen. Diese Art der Erklärung hat auch viel mehr Wahrscheinlichkeit für sich als die entgegengesetzte, wonach man die Bildung der Eiweißbausteine (Phenyl-alanin, Tyrosin u.s.w.) durch Einwirkung von Ammoniak auf die ungesättigte Säure ableiten will."

EXPERIMENTAL PART.

1. *Iodoacetic Acid Ethyl Ester*, $ICH_2CO_2C_2H_5$.[1]

Monochloroacetic acid ethyl ester prepared from monochloroacetic acid (from Kahlbaum) and using alcohol, conc. sulphuric acid as a catalyser, was transformed into monoiodoacetic acid ethyl ester. The fraction boiling at 178–180° was collected for the experiment. The yield of iodoacetic ester from chloroacetic ester was about 42%.

2. *Monoiodoacetic Acid l-Menthyl Ester*, $ICH_2CO_2C_{10}H_{19}$.

An equimolecular mixture of chloroacetic acid and menthol (Pharm. Jap.) purified by distillation, was heated at 120° for 6 hours and the product was treated with sodium carbonate and water successively to remove the free acid. The oily product was subjected to fractional distillation and the fraction boiling at 230–260° was collected. On standing, the oil solidified in a crystalline mass which crystallize from the alcoholic solution in fine needles melting at 37·2° and solidifying at 36·4°. Einhorn and Jahn[2] state 38° for its metting point.

The optical measurement of the ester was made in its alcoholic solution and the result is as follows:

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[1] Perkin, J. Chem. Soc., **65**, 428 (1894); Nef, Ann. d. Chem., **298**, 352 (1987).

[2] Arch. d. Pharm., **240**, 644 (1902); Chem., Zent., **74**, 399 (1903).

A solution of 0·1253 grm. of the ester made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0{\cdot}78°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -49{\cdot}80°$.

By the interaction of l-menthyl chloroacetate and potassium iodide in the alcoholic solution, l-menthyl iodoacetate was obtained. The ester purified by fractional distillation in vacuum was found to boil at 165–170° at 20 mm. E. Wedekind and O. Wedekind[1] state 165° at 22 mm. for its boiling point.

3. *Esters of α-Bromisovaleric Acid.*

α-Bromisovaleric acid, prepared according to Schleicher's method[2] from isovaleric acid and bromine, was transformed to the ethyl ester.

The l-menthyl ester[3] of the acid was also prepared from l-menthol and α-bromoisovaleric acid and the fraction boiling at 150–165° at 70 mm. was collected for the experiment.

4. *Dimethyl Phenyl Ethyl Acetate Ammonium Iodide,* $(CH_3)_2C_6H_5{\cdot}CH_2CO_2C_2H_5NI$.

When dimethyl aniline and ethyl iodoacetate were mixed together in molecular proportions there was formed a solid mass which, after washing with ether, was made to crystallize from the aqueous solution. It melts at 105° and soon solidifies to a mass melting at 215°.

Analysis of the substance gave the following value for iodine:

0·268 grm. substance gave 0·184 grm. AgI.

	Calc, for $C_{12}H_{18}O_2NI$.	Found.
Iodine	38·62	37·11

When pure ammonium salt was heated in a Jena-glass tube on a sulphuric acid bath, described in article III.,[4] it decomposed at 103·5° and then solidified.

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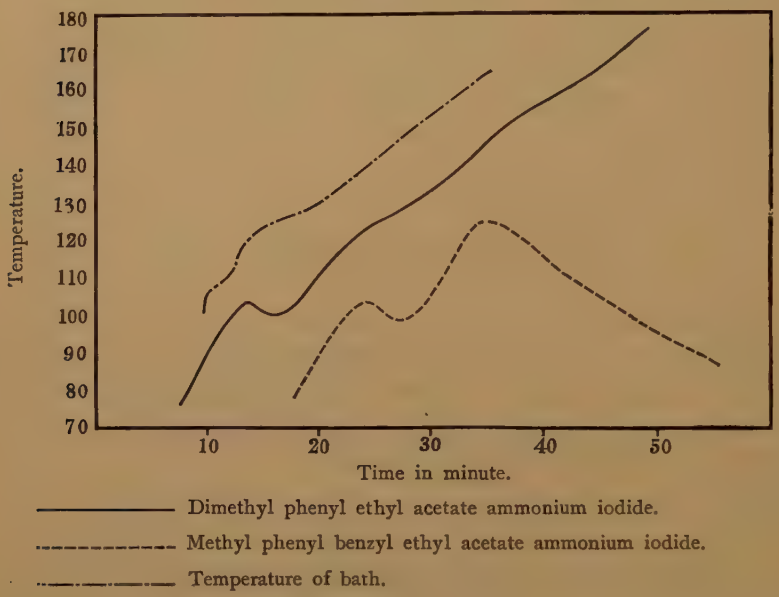
1 Ber. D. Chem. Gess., **41**, 456 (1908).
2 Lieb. Ann. d. Chem., **267**, 115 (1892).
3 Chem. Zentralbl., **80**, 1521 (1909).
4 These Memoirs, **1**, 246 (1915).

The thermal change of the substance was observed, and a curve was plotted with times and temperatures, as shown in Fig. I.

Fig. I.



From the fused mass above mentioned, trimethyl phenyl ammonium iodide was isolated. The substance, purified by the recrystallization from water, was analysed:

0·2162 grm. substance gave 0·1934 grm. AgI.

	Calc. for $C_6H_{14}NI$.	Found.
Iodine	48·29	48·34

The chloride prepared from the iodide obtained from the fused mass gave an insoluble yellow crystalline platinum double salt.[1]

0·1218 grm. substance gave 0·0355 grm. Pt on ignition.

	Cal. for $C_{18}H_{28}N_2Cl_6Pt$	Found.
Platinum	28·76	29·16

The fused dimethyl phenyl ethyl acetate ammonium iodide suddenly cooled with water was treated with ether. The etherial solution was then treated with dilute hydrochloric acid, and from the lower acidic layer of the solution dimethyl aniline was isolated, which was identified by the melting point of its picrate (mp. 155–156°).

[1] Hübner, Tölle u. Athenstädt, Ann. d. Chem., **224**, 352 (1884).

5. *Methyl Phenyl Benzyl Ethyl Acetate Ammonium Iodide,*

$CH_3 \cdot C_6H_5 \cdot C_7H_7 \cdot CH_2CO_2C_2H_5NI$.

It was prepared from methyl benzyl aniline and ethyl iodoacetate. The deposition of crystals began after 4 days consisting of a mixture of the two substances; and the yield of iodide after 8 days was about 25%.

It crystallizes from hot water in fine white needles melting at 115–116°. The substance is soluble in hot water and alcohol but not in ether.

I. 0·1053 grm. substance gave 0·2052 grm. CO_2 and 0·0478 grm. H_2O.
II. 0·2858 grm. „ „ 0·1587 grm. AgI.

	Calc. for $C_{18}H_{22}O_2NI$	Found.	
		I.	II.
Carbon	52·56	53·14	—
Hydrogen	5·35	5·05	—
Iodine	30·90	—	30·00

The ammonium iodide was transformed to the chloride by adding hydrochloric acid to the neutral substance produced from the iodide by treating with silver hydroxide, and then the chloride to the platinum double salt.

The platinum double salt melting at 155–156°, was dried at 100° for 2 hours and analysed:

0·1122 grm. substance gave 0·0255 grm. Pt on ignition.

	Calc. for $C_{32}H_{36}O_4N_2Cl_6Pt$	Found.
Platinum	21·20	22·70

When the substance was heated in a sulphuric acid bath, it was observed to decompose at 103°.

The fused substance was treated with ether, and from the etherial solution an oily substance, after distilling off the solvent, was obtained which was boiled with baryta water for 5 hours. On evaporating the filtrate, after removing the excess of baryta by carbon dioxide, barium salt of n-phenyl sarcosine was obtained which was dried at 110° for 3 hours and analysed:

0·2812 grm. substance gave 0·1391 grm. $BaSO_4$.

	Calc. for $(C_6H_5CH_3 \cdot N \cdot CH_2 \cdot CO_2)_2Ba$	Found.
Barium	29·52	29·12

Allowing 3 grm. of the melted mass to stand for a while, it solidified to a crystalline mass, from which 0·4 grm. pure original ammonium iodide melting at 114–114·5° was isolated.

For the confirmation of the recovered ammonium salt, its analysis and determinations of melting point and of its platinum double salt were conducted; and the results are shown as follows:

0·248 grm. substance gave 0·1403 grm. AgI.

	Calc. for $C_{18}H_{22}O_2NI$.	Found.
Iodine	30·90	30·66

0·0857 grm. platinum double salt melting at 145° gave 0·0184 grm. Pt on ignition.

	Calc. for $C_{32}H_{36}O_4N_2Cl_6Pt$.	Found.
Platinum	21·20	21·45

6. *Resolution of Methyl Phenyl Benzyl Ethyl Acetate Ammonium Iodide into its Optically Active Components.*

(A). *Methyl Phenyl Benzyl Ethyl Acetate Ammonium Dextro-Camphorsulphonate*, $CH_3{\cdot}C_6H_5{\cdot}C_7H_7{\cdot}CH_2CO_2C_2H_5N{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_{15}O$.

6 grm. pure methyl phenyl benzyl ethyl acetate ammonium iodide prepared from methyl benzyl aniline and ethyl iodoacetate, were boiled with 5 grm. silver dextro-camphorsulphonate in an acetone ethyl acetate solution over a water bath for 2 hours. After the reaction ended, silver iodide separated out; the solvent having been distilled off a syrupy residue was allowed to stand over sulphuric acid, solidifying in a crystalline mass. The crystalline mass thus formed was dissolved in acetone, from which white crystals were obtained. The substance was recrystallized from acetone 4 times, and the crystals melting at 178–179°, were analysed:

I. 0·1261 grm. substance gave 0·3295 grm. CO_2 and 0·0849 grm. H_2O.
II. 0·1559 „ „ „ 0·397 grm. CO_2 and 0·1038 grm. H_2O.
III. 0·2494 „ „ „ 0·1153 grm. $BaSO_4$.

	Calc. for $C_{28}H_{36}O_4NS$.	Found.		
		I.	II.	III.
Carbon	69·71	69 64	69·46	—
Hydrogen	7·47	7·48	7·40	—
Sulphur	6·64	—	—	6·35

The rotatory power of the pure specimen was determined in an aqueous solution with the following results:

(a). A solution of 0·3188 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}29°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +11{\cdot}37°$.

b). A solution of 0·2321 grm. substance obtained by recrystallization of the preparation (a) from acetone twice, made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = 0{\cdot}22°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +11{\cdot}85°$.

(c). A solution of 0·201 grm. substance obtained by recrystallization of the preparation (b) from ethyl acetate 4 times, made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}22°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +13{\cdot}68°$.

The ammonium iodide derived from the ammonium dextrocamphorsulphonate was observed to be optically inactive.

(B). *Methyl Phenyl Benzyl Ethyl Acetate Ammonium Bromide*, $(CH_3)(C_6H_5)(C_7H_7)(CH_2CO_2C_2H_5)NBr$.

By the action of potassium bromide on methyl phenyl benzyl ethyl acetate ammonium dextro-camphorsulphonate, methyl phenyl ethyl acetate ammonium bromide was obtained, which crystallizes in white needles from the aqueous solution, and melts at 139–140°. It is more soluble than the corresponding iodide.

The analysis of the substance gave the following results:

I. 0·1262 grm. substance gave 0·2797 grm. CO_2 and 0·0675 grm. H_2O.
II. 0·1466 grm. substance gave 0·0748 grm. AgBr.

	Calc. for $C_{18}H_{22}O_2NBr$.	Found.	
		I.	II.
Carbon	59·34	60·44	—
Hydrogen	6·04	5·94	—
Bromine	21·98	—	21·71

7. *l-Menthyl Acetate Pyridinium Iodide*, $CH_2CO_2C_{10}H_{19}C_5H_5NI$.

When pyridine (from Kahlbaum) and l-menthyl iodoacetate were mixed together in molecular proportions, there was immediately formed a solid mass with evolutien of heat which after washing with ether

was made to crystallize from hot water. The substance consists of the platy crystals and is soluble in hot water and alcohol, and melts at 178–179°.

The analytical results are as follows:

I. 0·3848 grm. substance gave 0·2161 grm. AgI.
II. 0·2117 grm. „ „ 0·3834 grm. CO_2 and 0·1314 grm. H_2O.

	Calc. for $C_{17}H_{27}O_2NI$.	Found.	
		I.	II.
Carbon	50·62	—	49·40
Hydrogen	6·45	—	6·89
Iodine	31·51	30·33	—

The optical measurement of the substance was made with the following result:

A solution 0·3733 grm. substance made up to 25 c.c. with alcohol at 25° gave $\alpha_D^{25} = -1·15°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -62·17°$.

By treating with silver hydroxide the substance was decomposed into menthol and optically inactive pyridine betaine, and the chloride of the latter gave a platinum double salt melting at 210–211°.

8. Formation of Methyl Phenyl Dibenzyl Ammonium Iodide from Methyl Benzyl Aniline and l-Menthyl Iodoacetate.

(A). *Methyl Phenyl Dibenzyl Ammonium Iodide,* $CH_3 \cdot C_6H_5(C_7H_7)_2NI$.

An equimolecular mixture of methyl benzyl aniline and l-menthyl iodoacetate was allowed to stand in a dark cold place for 4 months; then the crystals began to separate out from the solution. The substance, filtered from the solution and recrystallized from hot water, consists of the colourless prisms melting at 108·5–109°. It is soluble in hot water and alcohol. Its analysis is as follows:

I. 0·1493 grm. substance gave 0·3327 grm. CO_2 and 0·0793 grm. H_2O.
II. 0·294 grm. „ „ 0·166 grm. AgI.
III. 0·284 grm. „ „ 0·1587 grm. AgI.
IV. 0·2892 grm. „ „ 0·1639 grm. AgI.
V. 0·3655 grm. „ „ 0·204 grm. AgI.

	Calc. for $C_{26}H_{36}O_2NI$.	$C_{21}H_{22}NI$.	Found. I.	II.	III.	IV.	V.
Carbon	59·89	60·72	60·77	—	—	—	—
Hydrogen	6·91	5·30	5·90	—	—	—	—
Iodine	24·38	30·60	—	30·51	30·20	30·63	30·16

The substance is opitically inactive and converted into a basic substance by treating with silver hydroxide according to the details to be described hereafter.

Inferring from the analytical results, as well as from the chemical and physical properties, the author has to assume it to be methyl phenyl dibenzyl ammonium iodide.[1]

(B). *Methyl Phenyl Dibenzyl Ammonium Chloroplatinate,* $[CH_3 \cdot C_6H_5 \cdot (C_7H_7)_2 \cdot NCl]_2PtCl_4$.

It was formed by the interaction of platinic chloride and methyl phenyl dibenzyl ammonium chloride prepared from the corresponding iodide above mentioned; and it was found to melt at 137–138°.

The substance, dried at 110° for 2 hours, was analysed:

I. 0·1758 grm. substance gave 0·0349 grm. Pt on ignition.
II. 0·0767 grm. „ „ 0·0152 grm. „
III. 0·155 grm. „ „ 0·0304 grm. „

	Calc. for $C_{42}H_{44}N_2Cl_6Pt$.	Found. I.	II.	III.
Platinum	19·82	19·86	19·82	19·62

9. *Action of Pyridine on Ethyl α-Bromisovalerate.*

Pyridine (from Kahlbaum), mixed with an equivalent quantity of ethyl α-bromovalerate, was allowed to stand for 3 months in a dark cold place. No crystallizable reaction product was found to be formed; but on heating the mixture over a water bath for 5 hours, there separated out white platy crystals.

The crystals, separated from the mother liquor, and washed with ether, were analysed:

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1 Mem. Coll. Sci. Eng. Kyoto, **3**, 407 (1912).

0·263 grm. substance gave 0·31 grm. AgBr.

	Calc. for C_5H_5NHBr.	Found.
Bromine	50·00	50·20

The analytical result, melting point (207–208°) and other physical and chemical properties of the substance agree with those of pyridine hydrobromide described by Trowbridge and Diehl.[1]

From the filtrate from pyridine hydrobromide, the author has obtained a substance supposed to be ethyl dimethyl crotonate;[2] but the quantity of the material was so small that no close examination was possible.

10. Action of Pyridine on l-Menthyl Bromisovalerate.

3 grm. pyridine and 10 grm. l-methyl bromisovalerate were heated over a water bath for a while, by which process a white precipitate was formed. The product, separated from the mother liquor by filtration, was purified by steam distillation.

It was neutral to litmus and shown to be menthol by the analysis of a purified specimen.

0·1209 grm. substance gave 0·3414 grm. CO_2 and 0·166 grm. H_2O.

	Calc. for $C_{10}H_{20}O$.	Found.
Carbon	76·92	77·01
Hydrogen	16·14	16·17

Methylation of α-Aminoacids and Decomposition of α-Betaines by Heat.

11. Trimethyl p-Methoxy Phenyl Alanine,

$$CH_3O{\cdot}C_6H_4CH_2CH\!\!-\!\!-\!\!-\!\!-CO$$
$$\qquad\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad N(CH_3)_3\!-\!O.$$

Tyrosine used for the preparation of betaine was prepared from wheat protein by hydrolysis, and has the following nitrogen content, as determined by Duma's method:

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[1] Chem. Zentralbl., **68**, II. 592 (1897).

[2] C. A. Bischoff, Ber. D. Chem. Ges., **32**, 1755 (1899).

0.1365 grm. substance gave 8·6 c.c. N (14°, 764 mm.).

	Calc. for $C_9H_{11}O_3N$.	Found.
Nitrogen	7·7	7·5

According to Griess,[1] tyrosine was methylated with methyl iodide and caustic potash in the methyl alcoholic solution. When the reaction ended, the product was neutralised with dilute hydrochloric acid, p-methoxy cinnamic acid filtered, alcohol distilled off and the residue was treated with methyl alcohol 3 times to remove the inorganic salts. The solution was then evaporated to dryness and the betaine iodide thus formed dissolved in water and treated with "molecular" copper and cupric chloride to convert it into the chloride. After treating the filtrate with hydrogen sulphide to remove the copper salt remaining in the solution, the betaine was precipitated with potassium bismuth iodide (Dragendroff's reagent). The precipitate was then decomposed with lead hydroxide and the filtrate removed from the excess of the lead salts by means of hydrogen sulphide and silver hydroxide was evaporated to dryness. The betaine thus formed is a hygroscopic and forms picrate. The picrate consists of yellow needle-shaped crystals melting at 171–172°, and is soluble in alcohol.

The picrate, dried at 100° for 2 hours, was analysed:

0·098 grm. substance gave 0·1715 grm. CO_2 and 0·0506 grm. H_2O.

	Calc. for $C_{19}H_{23}O_{11}N_4$.	Found.
Carbon	48·60	47·72
Hydrozen	4·91	5·73

When the betaine was heated it decomposed into p-methoxy cinnamic acid and trimethyl amine.

The amine was purified by treating its hydrochloride with chloroform and found to be trimethyl amine by analysis and melting point (217–218°) of its double salt with platinum.

0·1745 grm. substance gave 0·0655 grm. Pt on ignition.

	Calc. for $[(CH_3)_3NCl]_2PtCl_4$.	Found.
Platinum	36·93	37·54

1 *Loc. cit.*

12. p-Methoxy Cinnamic Acid, $CH_3O\,C_6H_4CH:CHCO_2H$.[1]

The substance obtained from trimethyl p-methoxy phenyl alanine by heating crystallizes from hot water in fine white needles melting at 170–171°. The substance dried at 110° was analysed:

0·1154 grm. substance gave 0·2889 grm. CO_2 and 0·0584 grm. H_2O.

	Calc. for $C_{10}H_{10}O_3$.	Found.
Carbon	67·40	68·27
Hydrogen	5·62	5·62

The presence of the methoxy group in the substance was determined by Zeisel's method[2] with the following result:

0·2402 grm. substance gave 0·29 grm. AgI.

	Calc. for $CH_3O\,C_6H_4CH:CHCO_2H$.	Found.
CH_3O	17·41	15·94

13. p-Methoxy Hydrocinnamic Acid, $CH_3O{\cdot}C_6H_4CH_2CH_2CO_2H$.[3]

The substance prepared from p-methoxy cinnamic acid by reduction with sodium amalgam crystallizes from hot aqueous solution in white needles melting at 101–102°.

0·1144 grm. substance gave 0·2752 grm. CO_2 and 0·0704 grm. H_2O.

	Calc. for $C_{10}H_{12}O_3$.	Found.
Carbon	66·67	65·61
Hydrogen	6·67	6·84

14. Trimethyl Phenyl Alanine, $C_6H_5CH_2{\cdot}CH\!\!-\!\!CO$ (with $N(CH_3)_3$ and O)

The phenyl alanine used for this experiment was obtained by the hydrolysis of wheat protein, and gave the following analytical result:

0·1136 grm. substance gave 0·2679 grm. CO_2 and 0·0745 grm. H_2O.

	Calc. for $C_9H_{11}O_2N$.	Found.
Carbon	65·45	64·32
Hydrogen	6·64	7·28

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1 Eigel, Ber. D. Chem. Ges., **20**, 2530 (1887); Knoevenagal, *Ibid*, **31**, 2606 (1898).

2 Monats. f. Chem., **6**, 989 (1885); **7**, 406 (1886).

3 Abderhalden. Biochemisches Handlexikon. I., 1276.

The trimethyl phenyl alanine prepared from phenyl alanine by methylation as in the case of tyrosine, is hygroscopic.

The picrate of the betaine consists of prismatic crystals and melts at 162–163°.

The analytical result of the picrate is as follows:

0·1007 grm. substance gave 0·1818 grm. CO_2 and 0·041 grm. H_2O.

	Calc. for $C_{18}H_{21}O_9N_4$.	Found.
Carbon	49·43	49·24
Hydrogen	4·81	4·61

The betaine decomposes into trimethyl amine and cinnamic acid by heat.

The amine thus formed was identified by the analysis and melting point (215–216°) of its picrate.[1]

0·0731 grm. substance gave 0·101 grm. CO_2 and 0·0316 grm. H_2O.

	Calc. for $C_9H_{12}O_7N_4$.	Found.
Carbon	37·50	37·73
Hydrogen	4·19	4·81

15. Cinnamic Acid, $C_6H_5CH{:}CH{\cdot}CO_2H$.[2]

The substance prepared from trimethyl phenyl alanine by thermal decomposition was purified by recrystallization from its aqueous solution.

It was converted by addition of bromine to dibromocinnamic acid, and found to be oxidized readily in cold by potassium permanganate to benzaldehyde.

It melts at 130–131°, and was analysed:

0·1224 grm. substance gave 0·324 grm. CO_2 and 0·06 grm. H_2O.

	Calc. for $C_9H_8O_2$.	Found.
Carbon	72·93	72·20
Hydrogen	5·46	5·44

The barium salt of the acid dried at 110° for 3 hours and analysed gave the following result:

0·1254 grm. substance gave 0·0662 grm. $BaSO_4$.

	Calc. for $C_{18}H_{14}O_4Ba$.	Found.
Barium	31·79	31·05

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1 Rosenthaler: Der Nachweis Org. Verbindungen. 1914, p. 522.

2 *Ibid*, p. 322.

16. Dibromocinnamic Acid, $C_6H_5CHBr{\cdot}CHBr{\cdot}CO_2H$.[1]

On adding bromine to the carbon bisulphide solution of cinnamic-acid above mentioned, dibromocinnamic acid was formed. It melts at 195°, and was analysed:

0·2635 grm. substance gave 0·3225 grm. AgBr.

	Calc. for $C_9H_8O_2Br_2$.	Found.
Bromine	51·95	52·08

17. Trimethyl α-Amino Butyric Acid, $CH_3{\cdot}CH_2CH(N(CH_3)_3)—CO—O$.

The substance obtained from α-amino butyric acid (Kahlbaum) by methylation with methyl iodide and caustic potash in the methyl alcoholic solution, was separated as phosphotungstate from the other reaction products.

Its picrate consists of yellow needles melting at 155–156°, soluble in alcohol. Its analysis gave the following result:

I. 0·1092 grm. substance gave 0·1625 grm. CO_2 and 0·052 grm. H_2O.
II. 0·114 grm. „ „ 10 c.c. N (15°, 757·8 mm.).

	Calc. for $C_{17}H_{19}O_9N_4$.	Found.
Carbon	41·60	40·61
Hydrogen	5·07	5·29
Nitrogen	14·94	15·54

Such betaine was heated in a flask for a few hours, and whole the contents were subjected to distillation. The trimethyl amine formed as a decomposition product was identified by the analysis of its double salt with aurichloride.[2]

0·0779 grm. substance gave 0·0379 grm. An on ignition.

	Calc. for $C_3H_{10}NAuCl_4$.	Found.
Gold	49·37	48·65

18. α-Crotonic Acid, $CH_3CH{:}CH{\cdot}CO_2H$.[3]

By the thermal decomposition of the betaine of α-aminobutyric acid α-crotonic acid was obtained.

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1 A. Schmitt. Lieb. Ann. **127**, 320 (1863).
2 Rosenthaler: Der Nachweis. Organ. Verb., 1914. p. 522.
3 *Ibid.*, p. 303.

It was identified by the analysis of the free acid and its barium salt.

0·199 grm. substance gave 0·4036 grm. CO_2 and 0·1329 grm. H_2O.

	Calc. for $C_4H_6O_2$.	Found.
Carbon	55·81	55·31
Hydrogen	6·97	7·42

0·3383 grm. the barium salt gave 0·2505 grm. $BaSO_4$.

	Calc. for $(C_4H_5O_2)_2Ba$.	Found.
Barium	44·63	43·61

19. On the Methylation of Aspartic Acid.

Körner and Menozzi[1] obtained fumaric acid from aspartic acid by the action of methyl iodide and caustic alkali, and Dr. Yoshimura[2] has also recently observed that aspartic acid by the same process decomposes into fumaric acid and ammonia. The author in repeating their experiments, has observed the following facts:

When aspartic acid (from Kahlbaum) was heated over a water bath with methyl iodide and caustic potash in the methyl alcoholic solution in a flask provided with Dimrot's condenser, the reaction soon set in and the solution became neutral and finally acidic. A white crystalline substance then began to deposit on the inner wall of the condenser and trimethyl amine escaped from the condenser was collected in hydrochloric acid as usual. When the reaction ended, the product in the flask was acidified with dilute hydrochloric acid, by which process fumaric acid separated out, and the yield of the latter acid from 10 grm. aspartic acid was found to be about 4 grm.

The white crystalline substance deposited on the wall of the condenser and recrystallized from hot aqueous solution, was found to be tetramethylammonium iodide, which may have been formed by the interaction of methyl iodide and trimethyl amine, as supposed to be the decomposition products of the betaine of aspartic acid.

The ammonium iodide dried at 110° gave the following result by analysis:

---

1 *Loc. cit.*

2 *Loc. cit.*

I. 0·1283 grm. substance gave 0·1159 grm. CO_2 and 0·0979 grm. H_2O.
II. 0·1983 grm. „ „ 0·238 grm. AgI.

	Calc. for $C_4H_{12}NI$.	Found. I.	Found. II.
Carbon	23·83	24·54	—
Hydrogen	5·93	5·42	—
Iodine	63·18	—	63·95

20. *Fumaric Acid*, $\begin{matrix} CH\,CO_2H \\ \| \\ CH\,CO_2H \end{matrix}$ [1]

The substance was prepared from aspartic acid by the action of methyl iodide and caustic potash. It was recrystallized from hot aqueous solution, and gave the following result by analysis :

0·109 grm. substance gave 0·1645 grm. CO_2 and 0·0303 grm. H_2O.

	Calc. for $C_4H_4O_4$.	Found.
Carbon	41·38	41·16
Hydrogen	3·45	3·70

In conclusion, I wish to record my indebtedness to Dr. Shintaro Kodama, for his kind assistance in carrying out these experiments by supplying the samples of several amino acids.

[1] Rosenthaler. Der. Nachw. Org. Verb., 1914. p. 332.

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